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Bright Electroplating of Copper in the Acid Bath

Elwood K. Jensen

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Bright Electroplating of Copper
in the Acid Bath

A Thesis

Submitted to the Department of Metallurgy
in Partial Fulfillment

of the Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering

by

Elwood K. Jensen
Montana School of Mines
Butte, Montana

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ABSTRACT

A discussion of the theories and applications of bright copper electroplating is presented, and a number of recent investigations are described, particularly with reference to the results and conclusions obtained.

An attempt is made to duplicate the results shown by Clifton and Phillips², but this proves unsuccessful. Further experimentation yielded satisfactory plating, the optimum being realized in an electrolyte containing 150 grams CuSO_4 crystals, 10 grams H_2SO_4 , 15 grams $(\text{NH}_4)_2\text{SO}_4$, and 0.03 gram of thiourea, as well as 0.08 gram of Karo corn syrup, per liter of solution. This is found to yield a very fine-grained, smooth, bright deposit of the metal, which is the object of this thesis.

INTRODUCTION

The electroplating is now making rapid progress in developing cheaper and more effective methods of electroplating metals. The nature and properties of these deposits can be varied so that certain good qualities may be stressed, while other less desirable aspects may be minimized by proper electrolysis. The plating of various objects with mirror-like surfaces of chromium, nickel, and other metals has expanded considerably during the past decade, and now ranks as an important enterprise, particularly with respect to the automotive industry.

Acid copper plating was first mentioned in Smee's book, "Electro-Metallurgy", published in 1810. Within twenty years the process had found commercial application in the plating of ship hulls. Since that time the electrolyzing of this metal has found other uses in electroplating, electrorefining, and electrowinning. In the field of electroplating we find several important electroforming operations⁵, which include the following:

1. Electrotyping, or forming duplicate letterpress printing plates.
2. Sound and phonograph records. Winkler⁵ states:

"No product of the entire electroplating field so convincingly accentuates the exact and faithful reproduction in design, down to the finest detail, as does the finished phonograph record."

The principal steps involved in the manufacturing of these records are presented here as a flowsheet:

- A) Original wax or cellulose acetate record (+)
 - B) Master mold (electrodeposited copper (-))
 - C) Metal records (electrodeposited copper (+))
 - D) Metal stampers (electrodeposited (-) nickel, followed by copper)
 - E) Plastic playing records (+)
3. Master coin dies, embossing dies, etc.
 4. Duplicate printing plates for currency.
 5. Powder copper for powder metallurgy.
 6. Mirror reflectors.
 7. Thin sheet copper, seamless tanks, etc.
 8. In plating chromium on steel and zinc, a layer of copper must first be deposited, followed by a layer of nickel, then chromium.

Several electrolytes have been proposed for copper plating, each possessing certain definite advantages and disadvantages. At present the acid sulfate type, consisting essentially of CuSO_4 and H_2SO_4 , is the most prevalent; it offers the following advantages:

1. Dependability and stability of solution.
2. Its preparation is simple, rapid, and cheap.
3. Efficiencies at both electrodes approach 100 %.
4. High current density is possible, especially if the electrolyte is agitated.

However, it offers some disadvantages:

1. Difficulty is encountered in trying to plate copper on less noble metals, such as iron.
2. Electrolysis does not cleanse the cathode.
3. The plate is usually not bright, but dull.
4. The throwing power is poor, especially if much agitation is employed.

Another prominent type of copper-plating bath is the cyanide type. Its advantages include:

1. Copper can be plated on iron and similar metals.
2. The deposit is smooth and brighter than that obtained in the acid electrolyte.

The cyanide bath also has some disadvantages, as follows:

1. Current efficiencies are low at both electrodes.
2. The conductivity is lower than that of the acid type.
3. Closer control of the solution must be maintained.
4. The bath is much more toxic than the acid bath, and there is danger of poisoning from HCN gas.

Other types of electrolytes have been tried, but these have proven unsuccessful, in general; their practical application is precluded because of their low conductance and difficulty in control.

Besides the ordinary plating there is now a special field of bright plating, which has been practised with nickel and a few other metals for some time. Winkler⁸ says:

"If a brightener for the acid copper sulfate bath is discovered that will result in copper deposits comparable in appearance with that of bright nickel deposits, the use of acid copper solutions will receive a decided impetus."

In the same paper he also remarked:

"Various economic reasons such as the scarcity of cyanides, limitation of nickel supplies, etc., are causing at present an increase in the use of the acid copper plating bath."

These statements suggested a possible line of research, thus opening the way for this thesis, as will be seen later. Others have already begun work in this field of electrometallurgy.

SCOPE

This thesis is written with the purposes of corroborating certain recent investigations in the field of bright acid copper plating and ascertaining the optimum conditions for a bright electrodeposit.

Although numerous opportunities exist for research in other closely allied phases of electrometallurgy, no attempt is made herein to touch upon any of these subjects. Certain types of copper-plating baths, such as the oxalates, have not been studied extensively with a view toward the possibilities of bright plating. Cyanide baths, on the other hand, have been investigated more thoroughly, leaving less room for original research. The acid plating of copper on iron and zinc might be attempted, in an endeavor to eliminate the cyanide strike which is still used when depositing copper on these metals; the basic copper sulfate bath, as recommended by Greenspan⁷, might

be tested in this respect.

The acid copper sulfate type of electrolyte is the only one tested, and thiourea is the only brightening agent employed, although other addition agents were added for other purposes. Cathodes of copper, iron, and arsenic are examined; the anodic metal is copper at all times.

A rough comparison of the bright acid bath to other common copper-plating baths is given below:

TABLE I.

CLASSIFICATION OF COPPER-PLATING BATHS

Bath	Rochelle cyanide	Ordinary cyanide	High speed cyanide	Ordinary acid	Bright acid
Uses	incidental striking cleaning plating		plating	refining	plating
Tendency	declining	prevalent	starting	prevalent	starting
Efficiency	low	medium	high	high	high

It might be interesting to know why the bright bath yields a plate which differs so greatly from that usually obtained. For this reason an attempt is now made to explain this phenomenon.

THEORY

A bright deposit is defined as being one in which the specular reflection of the plated metal is superior to that of the basis metal. The brightness of the deposit can only be accounted for by the action of the addition agents. According to Henricks⁶ four theories have been proposed to account for this brightness:

- 1) The adsorption theory, which may be true in the case of certain colloidal substances such as gums and proteins. Because it cannot be explained satisfactorily, it is not generally accepted.
- 2) The reducing agent theory, which supposes that a reducing film forms about the cathode, the reducing agent tending to cause finer grains to form than could be produced if the film were of an oxidizing nature. The validity of this theory is questioned, since the reducing effect of any addition agent, in the amounts ordinarily employed, is small in comparison with that of the cathode, which manifests a strong reducing power even in the presence of powerful oxidizing substances.
- 3) The complex ion theory, which proposes the idea that the metal in the electrolyte forms a complex ion, which, in turn, yields a deposit having finer grains than could be obtained from simpler ions. This is

disproved by the cyanide type of bath, in which the deposit has coarser grains, in general, than that of the acid type.

- 4) The cathode interference theory, which states that if the ratio of the metal ion concentration in the cathode film to the concentration of the other film constituents is low enough (which may be due to the presence of colloids, complex ions, or adsorbed materials), there will be much interference with the growth of the copper crystals which form on the cathode, causing them to grow at a slower rate. When the rate of growth is decreased there will be a correspondingly greater number of crystals in the deposit. In this way the plate will consist of smaller but more numerous copper crystals.

Read and Graham² examined the electrolyte film which forms immediately adjacent to the cathode, and found that electrolysis caused the concentrations of the acid and of the copper ions in this film to differ from that of the main body of the electrolyte. These differences varied with various current densities, as the reader may observe in Figures I and II.

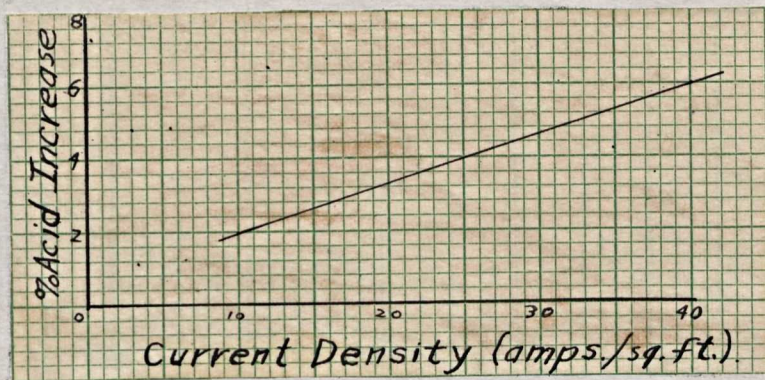


Figure I.

Relation of Current Density to Increase of Acid in Electrolytic Film.

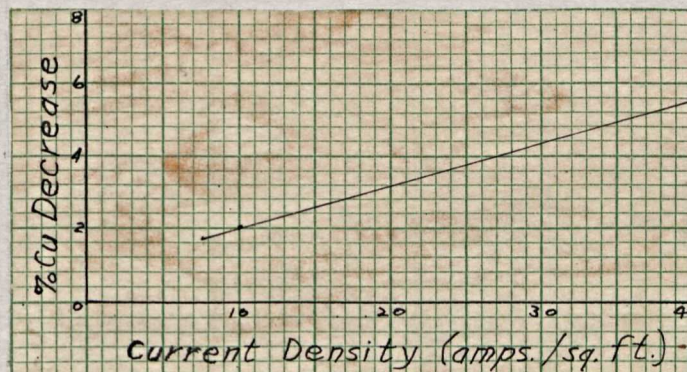


Figure II.

Relation of Current Density to Decrease of Copper Ions in Electrolytic Film.

The reason for the increase of acid concentration in the film is that hydrogen ions are attracted to the cathode by reason of their positive charge, but they cannot be evolved as a gas because of the low voltage. This increase in hydrogen ion concentration causes a corresponding fluctuation in the acidity. The decrease

in copper ion concentration is due to the removal of these ions as they plate out on the cathode as metallic copper.

Read and Graham also found that the difference in these concentrations diminished with rising temperature and with agitation. Their experiments also indicated that the composition of the film, under ordinary plating conditions, is practically the same at any point in the film. Since the composition of the main body of the solution is also regarded as being a constant, they concluded that the difference of these compositions is nearly always the same, this polarization being due to an equilibrium between the rate of diffusion and the rate of deposition. The effect of agitation may be seen by consulting Figure III below.

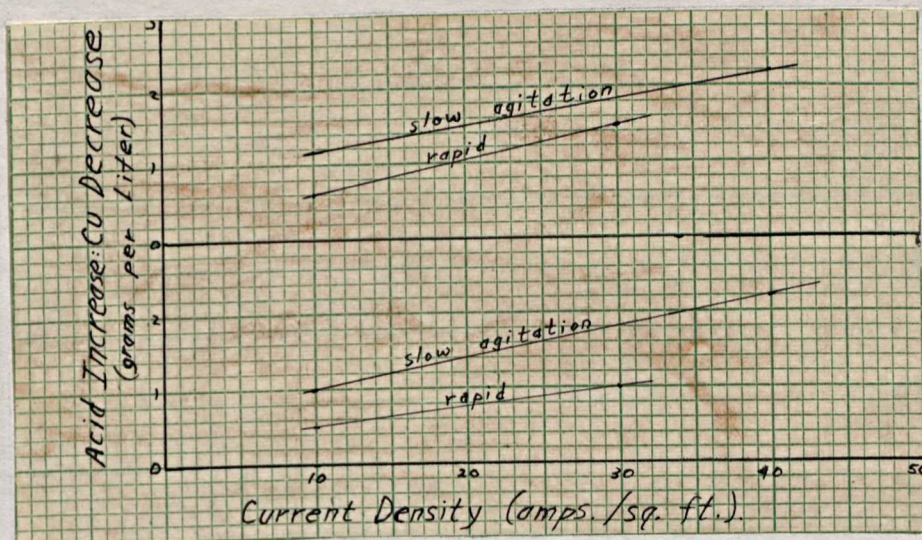


Figure III.

Effect of Agitation upon Variations of
Acid and Copper Ions at Different
Current Densities.

Other important features of the deposit include grain size and hardness. Butts and De Nora³ found that the grain size generally increases with higher temperature and metal ion concentration of the electrolyte, and that it usually decreases with greater current density, cathode polarization, and agitation. A certain amount of addition agent generally aids in decreasing grain size also, as may be seen later. Variations of the pH have no detectable effect upon grain size, but the surface condition of the base metal exerts some influence, the grain structure of the deposit being inclined to follow that of the basis metal. Figures IV and V illustrate the effects of temperature and current density on the grain size of the plated metal, while Figure VI indicates the general relationship between grain size and hardness.

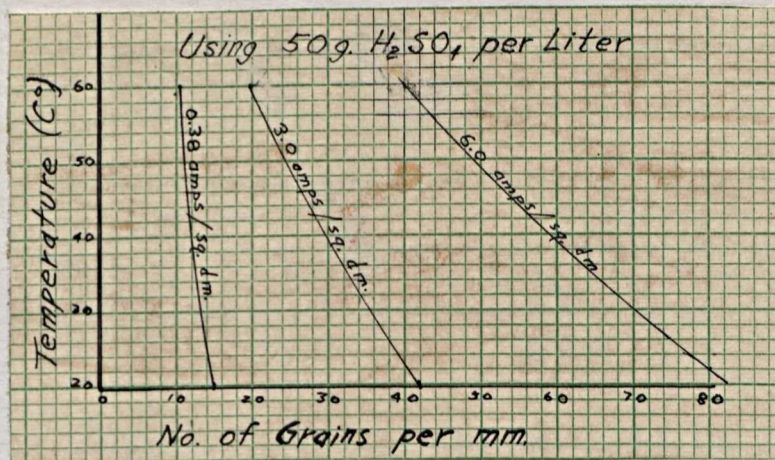


Figure IV.

Effect of Temperature upon Grain Size.

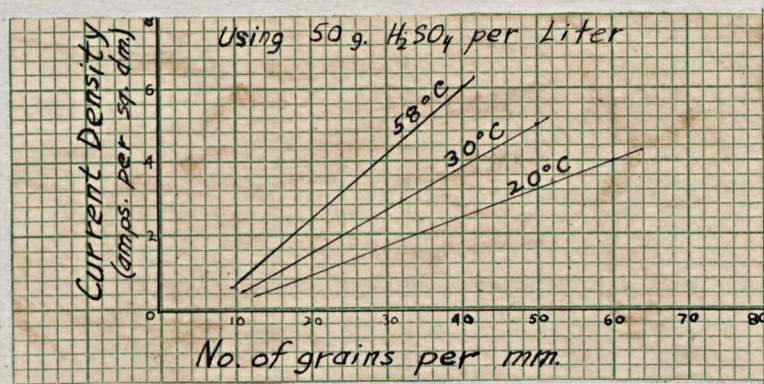


Figure V.

Effect of Current Density on Grain Size.

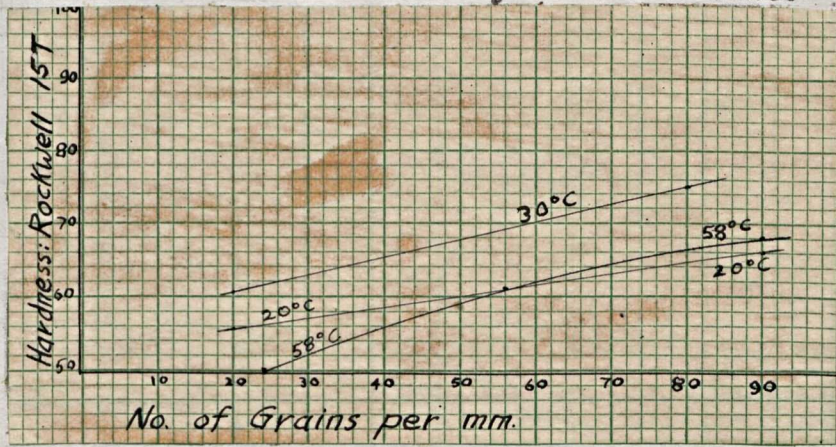


Figure VI.

Relation between Grain Size and Hardness.

The preceding discussion has been concerned with acid copper sulfate baths, in general, and the facts and relations can apply to both ordinary and bright plating types. Since our interest lies principally in the latter, we shall now confine our attention to this particular phase of the situation.

RELATED INVESTIGATIONS

Winkler⁷ first suggested the idea of bright copper plating in the acid bath, but he did not carry out any research along this line. However, he presented a simple, rapid, and accurate scheme for use in controlling the acid electrolyte. The specific gravity of the solution is measured to determine the amount of combined CuSO_4 and H_2SO_4 present (see Table II). A sample of the liquid is then titrated with standardized NaOH to ascertain the amount of acid, using methyl orange indicator. The CuSO_4 can then be found by difference.

Lawrence Greenspan experimented with a basic sulfate electrolyte in attempting to obtain bright copper plate; diethylene triamine was the only brightening agent employed. He found the optimum composition of the electrolyte to be:

CuSO_4 crystals	- - - - -	100 grams/Liter
$(\text{NH}_4)_2\text{SO}_4$	- - - - -	20 grams/Liter
Diethylene triamine	- - - - -	80 cc/Liter

The pH was maintained from 9.0 to 9.5, using aqua ammonia. His attempts were successful, but the conductance of the solution proved to be low.

Thiourea was advocated as a brightener by Clifton and Phillips², who experimented with an acid sulfate type of bath, using sulfonates, Triton

TABLE II.

TOTAL CONCENTRATION OF (CuSO_4 and H_2SO_4)
IN SOLUTIONS OF GIVEN SPECIFIC GRAVITIES.

Specific Gravity of solutions at 25° C.	Combined CuSO_4 and H_2SO_4	
	Grams/Liter	Ounces/Gallon
1.01 - - - - -	20 - - -	2.7
1.02	36	4.8
1.03	52	7.0
1.04	68	9.1
1.05 - - - - -	84 - - -	11.3
1.06	100	13.4
1.07	117	15.7
1.08	133	17.8
1.09	150	20.0
1.10 - - - - -	166 - - -	22.3
1.11	183	24.5
1.12	200	26.8
1.13	217	29.1
1.14	234	31.3
1.15 - - - - -	251 - - -	33.6
1.16	268	35.9
1.17	286	38.3
1.18	303	40.6
1.19	321	43.0
1.20 - - - - -	339 - - -	45.5
1.21	357	47.8
1.22	375	50.2
1.23	393	52.6

These specific gravities are based upon the specific gravity of water as being 1.00 at a temperature of 4° C. This table was taken from the National Bureau of Standards Scientific Paper No. 275.

compounds, and other organic addition agents. They found that thiourea (which is also known as thio-carbamide) will yield brighter deposits than any of the others which were tested. For maximum brightness they recommended the following solution:

CuSO_4 crystals	- - - - -	250 grams/Liter
H_2SO_4	- - - - -	10 grams/Liter
$(\text{NH}_4)_2\text{SO}_4$	- - - - -	20 grams/Liter
Syrup or molasses	- - - - -	0.03 gram/Liter
thiourea	- - - - -	0.03 gram/Liter

Optimum conditions were found to include a temperature of 55° Fahrenheit, a current density from 35 to 45 amperes per square foot of cathode surface., and violent agitation. The electrolyte must be kept free from any trace of chloride ion, as this eliminates brightness of the deposit. Ammonium sulfate serves as a "range increaser", i.e., it allows a greater digression from the optimum without materially diminishing the brightness of the plate. Syrup or molasses is found to aid in forming a smoother, finer-grained deposit, and in reducing the striation tendency of the plated metal.

The results shown by Clifton and Phillips appear to be very favorable; in the light of their success an attempt is made to duplicate them. However, a word concerning the equipment, reagents, and other pertinent factors will first be presented.

EXPERIMENTAL PROCEDURE

These experiments were conducted with the purpose of obtaining the brightest plate of copper that could be produced in the acid sulfate bath, using thiourea as a brightening agent. The optimum and limiting conditions were to be studied and recorded.

The experiments were conducted in 600-cc Pyrex beakers, using 500-cc samples of each electrolyte which was prepared. Copper anodes and cathodes were cut from Anaconda electrolytic sheet copper, each electrode measuring 2 by 5 inches. Small wooden brackets held the electrodes parallel to each other at a distance of $1\frac{1}{4}$ inches. In some tests an iron cathode was used, this being cut from a thin sheet of pure, low-carbon steel. Before each electrolysis the copper electrodes were thoroughly cleansed with concentrated nitric acid, then rinsed with distilled water. The iron cathode was cleaned with hydrochloric acid, then rinsed in distilled water also. Agitation was provided by an electric stirring device, the activation being transmitted through a glass rod which dipped into the solution.

A simple electrical circuit was employed, as may be seen in Figure VII.

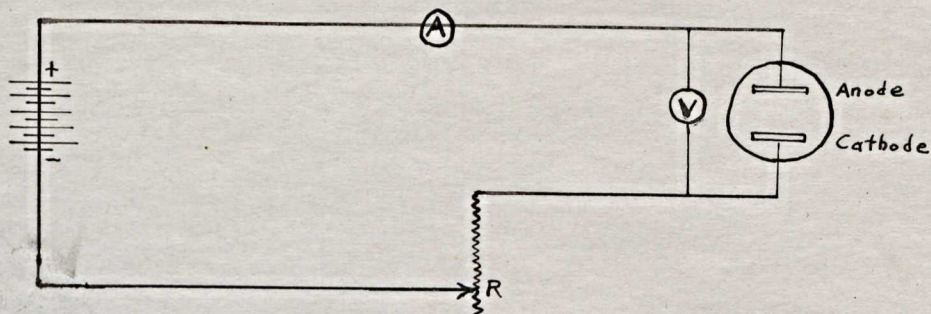


Figure VII.

Electrical Circuit Used in Electrolysis.

Only chemically pure reagents were used except where noted. Distilled water was used at all times, the tap water being rejected because of the possibility of its containing chlorides. The greatest care was taken to prevent contamination of the electrolyte, and to obtain the best possible deposit.

All tests were carried on for 30-minute periods except in some instances when anodic coating developed, which automatically shut off most of the current, as will be discussed later. Ordinary room temperature (60 to 70° Fahrenheit) was used except where otherwise indicated; in such instances an electric heating coil was employed to attain the desired heat.

Four series of tests were made before the proper results were finally obtained, the first two having baths which contained 250 grams of blue vitriol per liter, while that in the last two was 150 grams per liter. For the sake of simplicity these are

termed the high and low copper baths, respectively.

The High Copper Bath

A 500-cc sample of an ordinary acid sulfate bath was made up of the following constituents:

CuSO_4 crystals - - - - - 250 grams/Liter
 H_2SO_4 - - - - - 10 grams/Liter
 $(\text{NH}_4)_2\text{SO}_4$ - - - - - 16 grams/Liter

Using this solution and copper electrodes, the results shown in Table III were obtained. Ordinary room temperature and medium agitation were employed.

TABLE III.

RESULTS OF FIRST SERIES OF ELECTROLYSES

Test Number	Current density (amps./sq.ft.)	Cell Voltage	Nature of Deposit
1	30	1.47	Rough and dull Blue crystals form on anode, stop deposit.
2	40	2.55	Same as above
3	50	3.0	Same as above
4	55	3.2	Same as above

A second series of tests was made, the conditions being identical with those of the previous ones except for the composition of the solution, which is presented on the following page.

CuSO_4	- - - -	250 grams/Liter
H_2SO_4	- - - -	10 grams/Liter
$(\text{NH}_4)_2\text{SO}_4$	- -	16 grams/Liter
Thiourea	- - -	0.04 gram/Liter
Gelatin	- - -	0.03 gram/Liter
Karo syrup	- -	0.03 gram/Liter
Glue	- - - -	2 drops/Liter

This bath is almost the same as that employed by Clifton and Phillips except for the addition of small amounts of gelatin, Karo syrup, and glue. The results of the tests, using this bath, are given in Table IV, and the nature of the deposit can readily be seen by referring to Plate I, which is a photomicrograph of a section of the finished cathode. The rough nature of the deposit is partly due to electrolysis, and partly due to roughness in the polishing wheel used in the preparation of the photographed specimen.

The Low Copper Baths

Since the high copper baths contained an excessive quantity of CuSO_4 , an endeavor was made to remedy the situation by preparing electrolytes containing a lesser amount of this salt. The first electrolyte prepared contained the reagents listed on page 23. The third series of tests was performed with this bath, yielding the data in Table V; both electrodes were made of copper.

TABLE IV.

RESULTS OF SECOND SERIES OF ELECTROLYSES

Test Number	Current density (amps./sq.ft.)	Cell Voltage	Temperature	Nature of Deposit
1	10	0.75	60°F	Speckled, dull
2	20	1.5	60	Vertical striations; bright edges
3	30	2.3	60	bright edges
4	40	2.1	90	xtals. on anode
5	50	3.3	100	striations dull deposit
6	60	4.1	105	striations; dull deposit
7	70	3.8	110	dendritic streaks dull deposit
8	80	4.3	115	dendritic streaks dull deposit

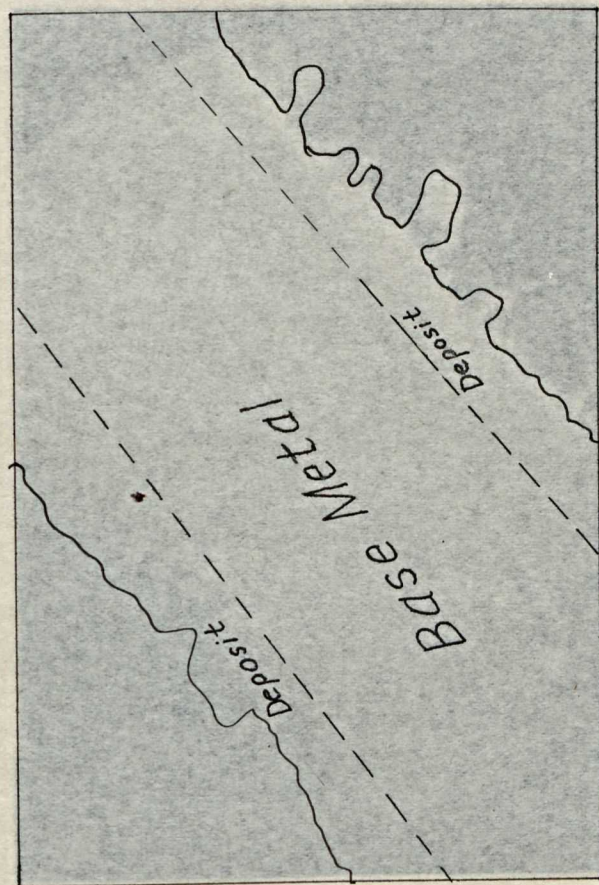


PLATE I.

Photomicrograph of Copper Cathode Obtained from
High Copper Bath (75X).

(Etched 1 minute with equal parts of 2% H_2O_2
and concentrated NH_4OH)

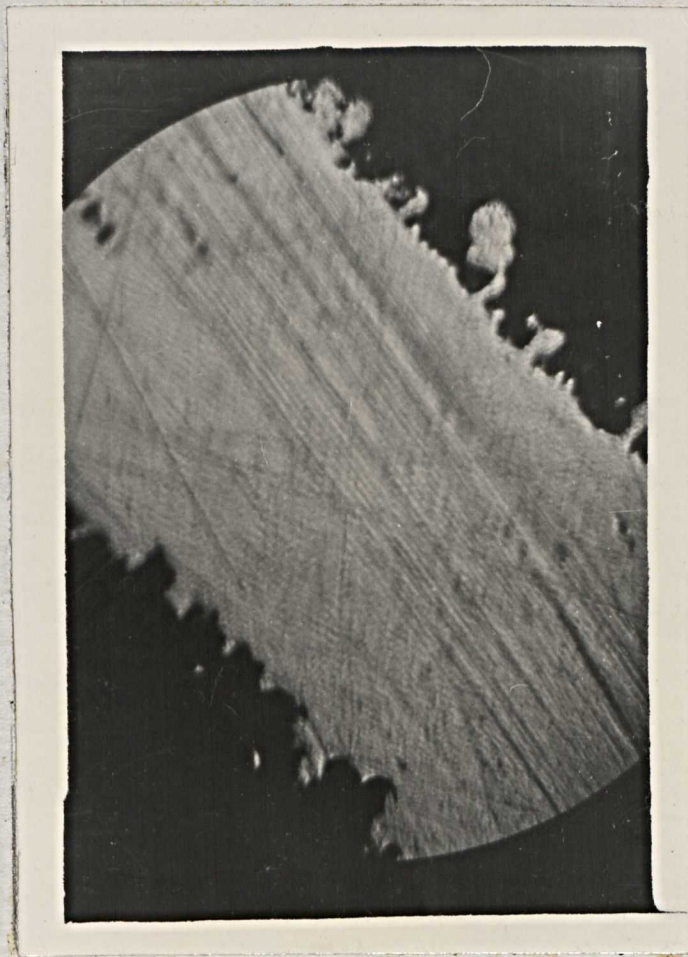


PLATE I.

Photomicrograph of Copper Cathode Obtained from
High Copper Bath (75X).

(Etched 1 minute with equal parts of 3% H_2O_2
and concentrated NH_4OH)

CuSO_4	- - - -	150 grams/Liter
H_2SO_4	- - - -	10 grams/Liter
$(\text{NH}_4)_2\text{SO}_4$	- -	2 grams/Liter
Thiourea	- - -	0.03 gram/Liter
Dextrose	- - -	0.03 gram/Liter
Glue	- - - -	2 drops/Liter

This electrolyte yielded the results below:

TABLE V.

RESULTS OF THIRD SERIES OF ELECTROLYSES

Current density (amps/sq.ft.)	Cell Voltage	Relative Agitation	Temper- ature	Nature of Deposit
30	2.8	rapid	65°F.	semi-bright and smooth
30	2.8	medium	65°F	smooth, dull
30	2.8	none	65°F	bright edges smooth, dull
30	1.4	medium	55°C.	fine-grained smooth, dull
40	1.7	rapid	55°C.	fine-grained smooth, dull

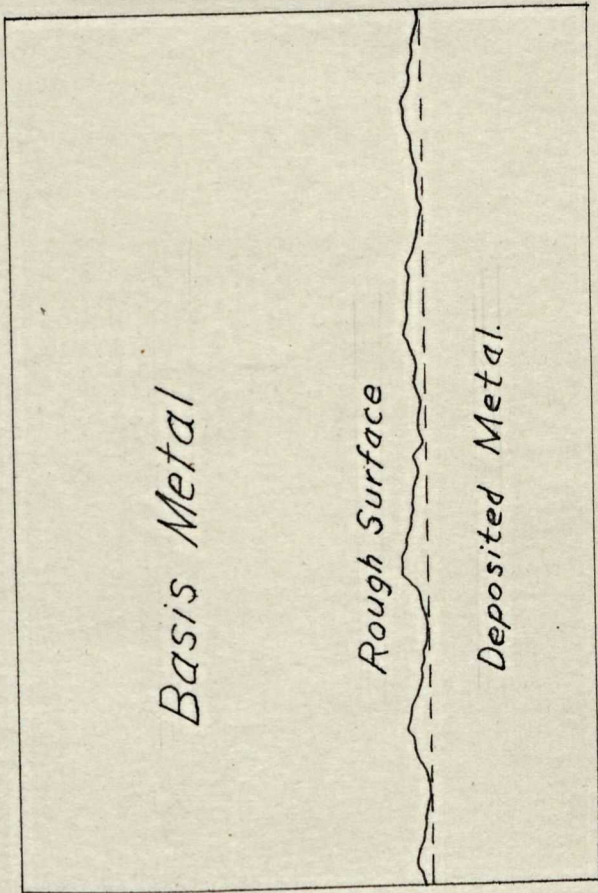
The deposits in this series were smooth and fine-grained, but lacked the bright luster which should have been present. The deficiency in ammonium sulfate may account for this; accordingly, a fourth solution, containing more of the salt, was made up as follows:

CuSO_4 crystals	- - - - -	150 grams/Liter
H_2SO_4	- - - - -	10 grams/Liter
$(\text{NH}_4)_2\text{SO}_4$	- - - - -	15 grams/Liter
Thiourea	- - - - -	0.03 gram/Liter
Karo corn syrup	- - - -	0.08 gram/Liter

Several tests were made with this bath, using copper electrodes, room temperature, and a current density of 40 amperes per square foot of cathode surface. The pH of the bath was found to be 0.9. These deposits were bright and smooth, despite the fact that some of the basis surfaces were rough, as may be seen from Plate II. The brightest plate was obtained when a rolled cathode was used, since the electrode presented a much smoother basis for electrodeposition, as may be seen by consulting the photomicrograph in Plate III.

Another bath was made up identical to the one just described except that the CuSO_4 was not c.p. but was of technical grade. Subsequent tests yielded copper plating comparable in brightness with that which was derived from the use of the pure salt. Using this same solution, an attempt was made to plate out copper on an iron cathode; this proved unsuccessful, however, since the deposit was bodily removed almost as rapidly as it formed, by the hydrogen which was liberated. In a short time a large quantity of metallic copper precipitated to the bottom of the cell and the iron surface remained practically uncoated.

An arsenic cathode was prepared by dipping a clean iron electrode into a solution containing 60 grams of As_2O_3 per liter of concentrated HCl, the arsenic forming a coating on the iron by replacement. Electrolysis was undertaken in a fresh



Basis Metal

Rough Surface

Deposited Metal.



PLATE II.

Photomicrograph of Bright Copper Plate

Deposited on Rough Cathode (75X).

(Etched 1 minute with equal parts 3% H_2O_2

and concentrated NH_4OH)

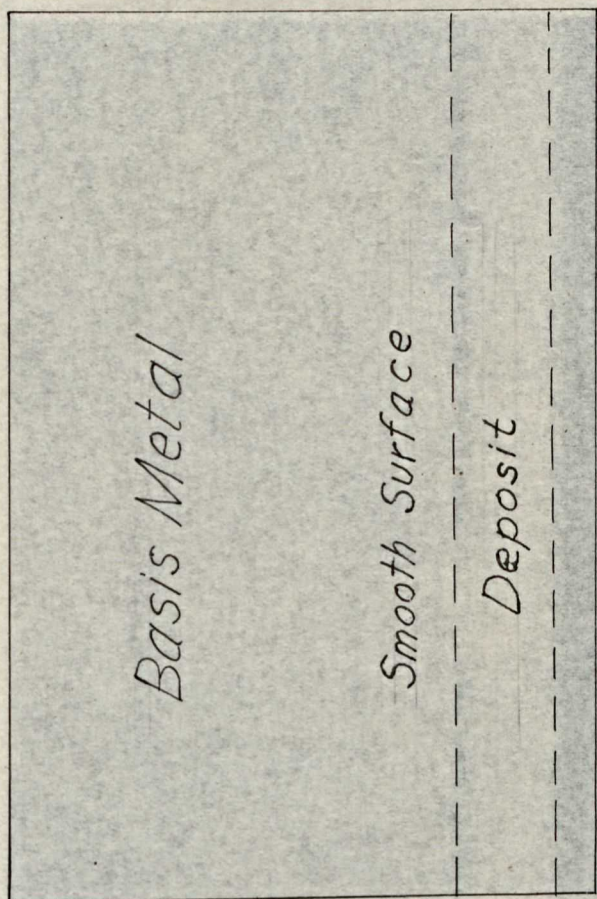


PLATE VII
Photomicrograph of Bright Copper Plate
deposited on Smooth Cathode (75X)
obtained for 1 minute with equal parts
of 3% H_2O_2 and concentrated NH_4OH .

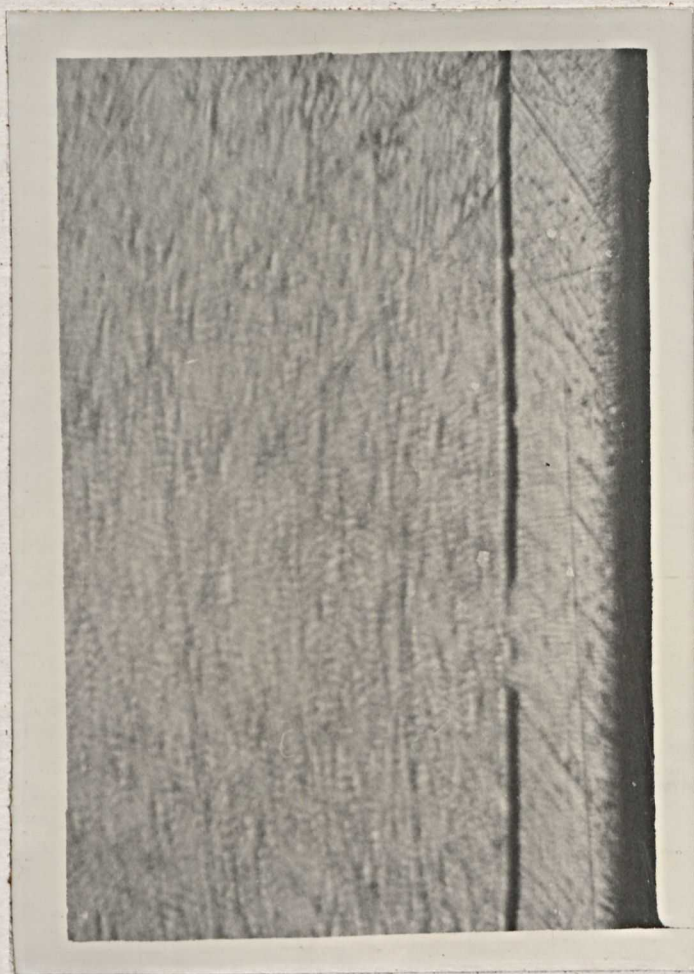


PLATE III.

Photomicrograph of Bright Copper Plate
Deposited on Smooth Cathode (75X)
(Etched for 1 minute with equal parts
of 3% H_2O_2 and concentrated NH_4OH)

bath having the composition shown at the bottom of page 23. Although the copper plated out smoothly and brightly at first, this did not continue very long because of minute cracks in the arsenic coating which allowed the electrolyte to come into contact with the iron base metal. Hydrogen was soon evolved at such points, this serving to detach the arsenic coating and the plated copper. Repeated trials proved unsuccessful, due to the difficulty of completely covering the iron surface with arsenic; these trials concluded the experimentations. Since an explanation of the results is now in order, the following discussion is presented with the idea of clarifying the situation.

RESULTS

The first series of tests proved unsuccessful because of the formation of crystals on the anode. While the exact formula is not established, the salt is believed to be a double sulfate having the general formula: $\text{CuSO}_4 \cdot (X)(\text{NH}_4)_2\text{SO}_4 \cdot (Y)\text{H}_2\text{O}$. Since this salt is less soluble than either of its separate constituents, the solution may easily become supersaturated, causing some of the compound to crystallize out. The reason for its formation on the anode is that the sulfate ion concentration is greatest in this vicinity, and the cupric ion

concentration is also strongest at this point because the anode is going into solution. The salt tends to form on the anode in a thin layer, eventually covering the surface almost completely, which causes the current to drop off, the conductance of the double salt being much lower than that of the bath.

This trouble persisted in the second group of tests, especially at the lower temperature. The double sulfate was dissolved completely by raising the temperature; upon doing this, however, the brightness of the plate was found to be diminished. A few traces of bright plate around the edges of the cathode indicated that a higher current density might yield a uniformly bright surface; this was later proven to be true within certain limitations.

In order to prevent the formation of any crystals of the double cupric ammonium sulfate, the copper and ammonium concentrations were both lowered for the third series of electrolyses. Best results were obtained at room temperature, but the brightness was again limited to the edges of the cathode, indicating that a higher current density might be advisable. Parenthetically, the current density is greatest at the edges and corners of the electrodes because these portions are exposed to a greater volume of solution per unit of area of metallic surface than any other portion of the electrode. When the current density is too low, the plate becomes striated, or streaked; if it is too high,

the deposit assumes a burned appearance. These deposits were not bright because of low current density and insufficient ammonium sulfate.

The fourth and fifth electrolyses proved to be successful, enabling bright coatings to form. The ammonium sulfate concentration was high enough to insure its effectiveness as a range increaser, while that of the CuSO_4 was correspondingly low enough to prevent any formation of the double salt.

The exact function of the addition agents, including thiourea, gelatin, syrup, dextrose, and glue is not fully understood. The most logical explanation for their influence is the cathode interference theory, which has been stated.

Thiourea (also called thiocarbamide) has the formula NH_2CSNH_2 ; it is known as an acid inhibitor in the sense that it is inclined to be basic, thus inhibiting the effect of the acid with which it may come in contact. In this way it may tend to reduce the percent increase of acid in the cathodic film.

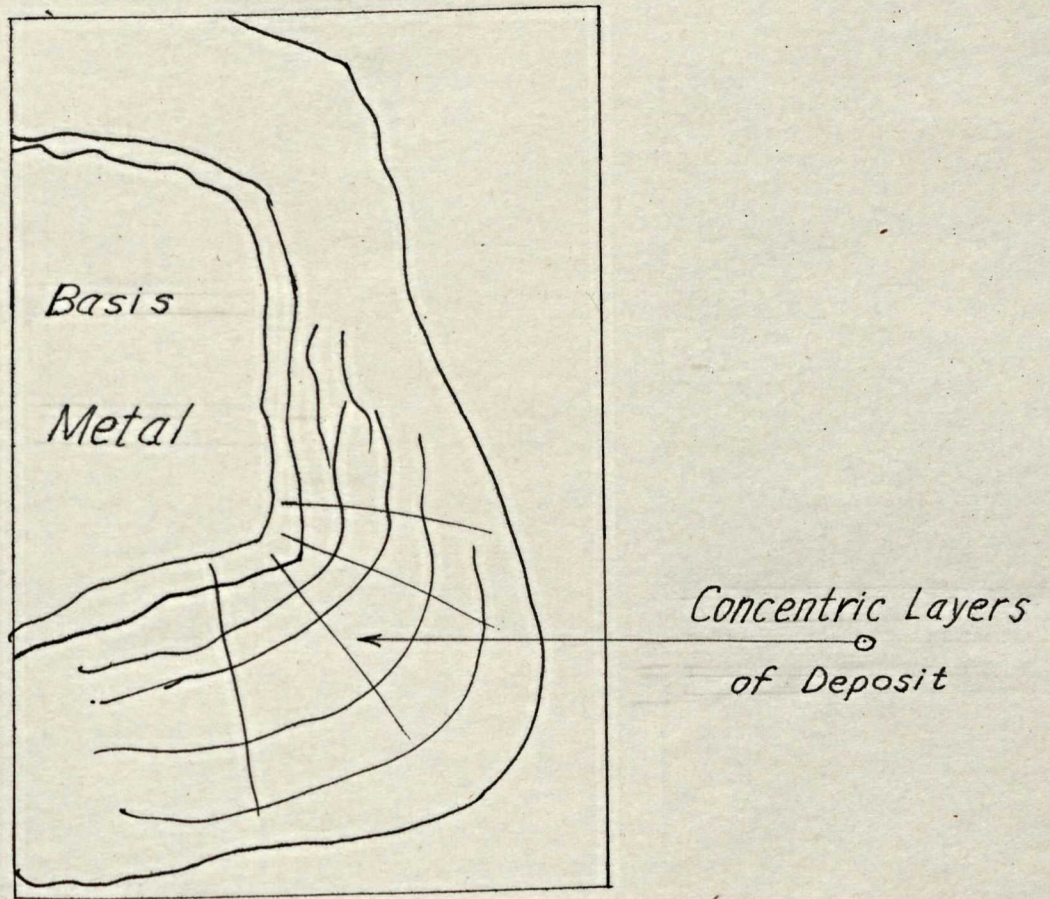
Karo corn syrup was used in order to obtain a finer, smoother deposit, and to reduce striation and embrittlement of the cathode. It consists of 85% glucose, the remainder being dextrin and molasses.

The sulfuric acid should be chemically pure⁹, while the CuSO_4 need not be of such high quality, since more of the salt is formed at the expense of the acid, this being caused by some of the anodic metal going into solution in the cuprous state, then

reacting with H_2SO_4 and oxygen to form CuSO_4 and water. The acid content must be regulated within certain limits, since a deficiency lowers the conductance, while an excess attacks the cathode as well as the anode, ruining the deposit and causing it to peel off.

In contrast to ordinary acid plating, wherein the plated metal tends to follow the grain structure of the basis metal, the bright plate exhibits no such tendency, the grains being inclined to form in layers parallel to the surface, as can be seen from Plates II and IV, the latter also illustrating the nature of the formation at the edge of the cathode. The poor throwing power of the solution is shown by the greater thickness of the deposit on the side nearest the anode as compared with that on the far side. There is no continuation of the grain structure of the base metal to be found in the deposit; some scratches, due to the polishing of the specimen, may be misleading in this respect:

It is believed that a thin layer of bright copper is first deposited, the bright surface then adsorbing a small amount of brightening agent from the adjacent film, the adsorbed layer being of monomolecular thickness. Further deposition of bright copper, which consists of very fine crystals of the metal, is effected upon the surface of the freshly adsorbed agent. Each unit layer of metal, while quite thin,



This side was nearest the Anode.

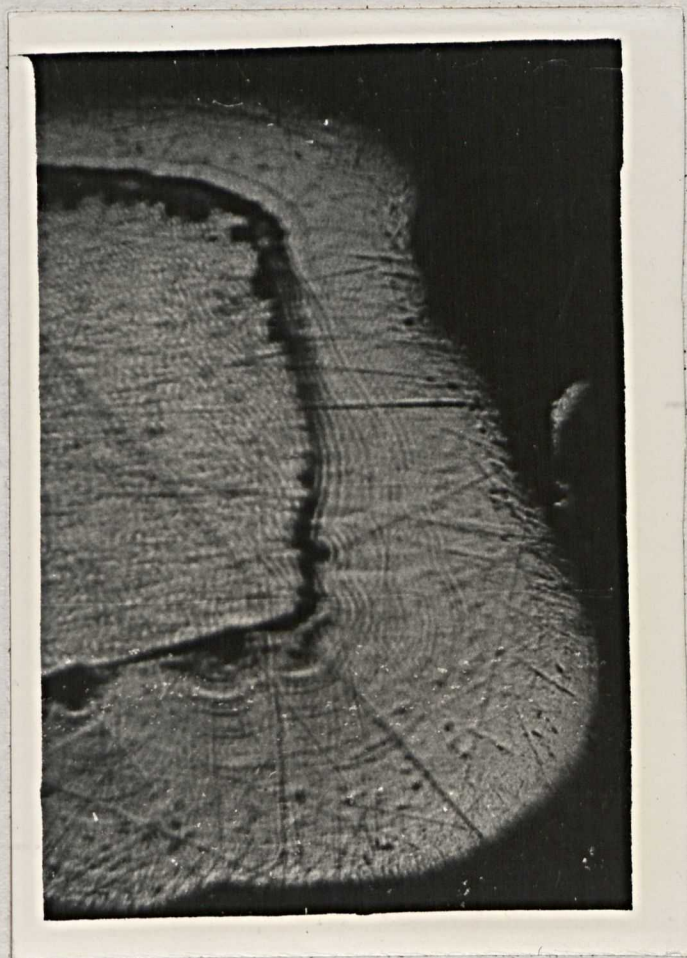


PLATE IV.

Photomicrograph of Bright Copper Deposit

Formed Around Edge of Cathode (75X)

(Etched 1 minute with equal parts of

3% H_2O_2 and concentrated NH_4OH)

is not believed to be of mere monomolecular thickness. This seems to be a logical assumption, since it agrees with the photomicrographic evidence^x shown in Plate IV.

CONCLUSIONS

A number of conclusions can be drawn from the preceding evidence; those which corroborate the findings of previous investigators include the following:

1. The electrodeposited metal formed in this bright acid bath is comparable in brightness with that obtained from bright cyanide solutions, the acid type being preferred because of its greater economy, higher conductance, ease of preparation and control, and less toxic nature.

2. The finer grains and smoother deposit which are obtained with this type of electroplating make it especially applicable to electroforming, as well as a base coating in bright chromium plating.

x - All photomicrographs were made by mounting the specimens in lucite plastic, grinding and polishing until smooth; representative surfaces were obtained. Each specimen was photographed through a 75X metallographic microscope, using an Argus 35-mm camera. The exposures were made at f4.5, 1/25 second, using Eastman Panatomic-X film, which was developed in Eastman DK-20 finegrain developer. Final prints were made on Eastman Kodabromide F-3 paper. Plate I is enlarged 5 diameters, the others being enlarged 8 diameters.

3. A certain amount of ammonium sulfate must be present to insure the brightest possible deposit; this salt functions as a range increaser.

In addition to these conclusions, a few original ones were drawn, including the following:

1. No particular brightening effect is produced by any addition agent employed, with the exception of thiourea, which produces a pronounced effect.

2. The bright deposit will have a greater hardness than the basis metal because of the smaller grain size of the former.

3. Successful bright copper plating can be effected in the acid sulfate bath if thiourea is present in amounts from 0.025 to 0.035 gram per liter of solution, and if the bath contains approximately 150 grams of CuSO_4 , 10 grams of H_2SO_4 , 15 grams of $(\text{NH}_4)_2\text{SO}_4$, and a trace of Karo syrup or molasses per liter.

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